



Non-trivial topological surface states regulation of 1 T-OsCoTe₂ enables selective C–C coupling for highly efficient photochemical CO₂ reduction toward C₂₊ hydrocarbons

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ABSTRACT

Despite ongoing research, the rational design of non-trivial topological semimetal surface states for the selective photocatalytic CO₂ conversion into valuable products remains full of challenges. Herein, we present the synthesis of lattice-matched 1 T-OsCoTe₂ for the photoreduction upgrading of CO₂ to tri-carbon (C₃) alkane (propane, C₃H₈) by the integration of experimental work and theory prediction/calculation. Experimental studies suggested a high electron-based selectivity of 71.2 % for C₃H₈ and an internal quantum efficiency of 54.6 % at 380 nm. In-situ X-ray photoelectron spectroscopy and X-ray absorption fine structure spectroscopy demonstrated that Co and Os atoms coordinated with Te atoms enable an efficient Os–Te–Co electron transfer to activate the generation of *CH₃, *CHOCO and *CH₂OCOCO. Density functional theory calculations further confirmed Os–Te–Co electron bridging on the improved CO₂ conversion kinetics. To our knowledge, this is the first report suggesting the role of Os atoms in accelerating the photocatalytic CO₂ conversion activity of the topological semimetal 1 T-OsCoTe₂.

1. Introduction

The surface states of catalysts, in which charge transport and reactant conversion occur simultaneously, plays a central role compared to the bulk state in determining its catalytic performance [1,2]. However, the surface states of catalysts are easily affected and disrupted by the adsorption and desorption of intermediates, fluctuations of surface defects, and potential changes during photoelectrochemical reactions. As time goes on, this dilemma can be skillfully resolved via establishing non-trivial topological surface states (TSSs), which are energy band structures protected by the bulk symmetry. Under this unique protection, the TSSs are unaffected by surface modifications and multiphase catalytic defects, enhancing the activity and stability of the catalysts [3,4]. Moreover, the energy dispersion relation of the non-trivial TSSs

results in extremely high carrier mobility and an exotic partial density of states (PDOS), which is crucial for promoting fast catalytic reactions [5,6].

1 T-CoTe₂, a typical type-II Dirac semimetal of transition metal-sulfide compounds, has been at the frontier of electrocatalytic research due to its diverse phase structure and ultrahigh carrier mobility [7,8]. More specifically, Co²⁺ sites play a crucial role in improving the selectivity of multi-carbon (C₂₊) hydrocarbons, which can not only accelerate the adsorption of *CO and promote the C–C coupling reaction but also stabilize the critical intermediates for generation of C₂₊ hydrocarbons [9,10]. Unfortunately, it remains a challenge for achieving satisfied products selectivity and internal quantum efficiency (IQE) due to the complex multiple-electron reduction in the CO₂ reduction reaction (CO₂RR) process. The introduction of another doping metal is an

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effective way to regulate and improve the stability of Co^{2+} , while the difference in atomic radii between the heteroatom and the Co atom causes lattice distortion, which affects the d -band center of the catalyst and thus changes the binding ability of the reaction intermediates on the catalyst surface [11]. More importantly, the doping metal also affects the activity of the competitive hydrogen evolution reaction (HER) [12]. Therefore, modulation of $^*\text{CO}$ binding energy and suppression of HER are essential objectives in developing metal-atom doped Co-based catalysts.

Based on the considerations mentioned above, integrating the advantages of a topological semimetal (1 T-CoTe₂) unit with robust surface states and a normal semiconductor (2 H-OsTe₂) unit into one alliance would be of great interest to optimize their potential for high-performance CO₂RR. In this paper, for the first time, we present a detailed investigation of the electronic structure and catalytic mechanism of 1 T-OsCoTe₂ via combining first-principles calculations with in-situ X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure spectroscopy (XAFS) experiments. The investigations demonstrate that the synergy between Co and Os metal sites is crucial for enhanced photocatalytic CO₂RR performance. Specifically, Co atoms act as the active catalytic sites, while adjacent Os atoms serve as promoters, and Te atoms function as the transport bridge facilitating electron flow. Density functional theory (DFT) calculations corroborate the strong orbital coupling between Os and Co atoms, causing the d -band structure with improved photoactivity. In-situ diffuse reflectance-infrared Fourier-transform spectroscopy (DRIFTS) combined with theory calculations reveal that the synergistic effect of Os and Co metal sites as well their Te electron bridging not only reduces the reaction barrier for the formation of $^*\text{CHOCO}$ and $^*\text{CH}_2\text{OCOCO}$, but also retards undesired HER, synergistically boosting CO₂ conversion to propane (tri-carbon (C₃) alkane, C₃H₈).

2. Experiment section

2.1. Materials and reagents

Tellurium powder (Te, more than 200 mesh) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Cobalt powder (Co, 99.99 %) and Osmium powder (Os, 99.99 %) were used without further purification. 5,5'-dimethyl-1-pyrroline N-oxide (DMPO) furnished by Shantou Xilong Chemical Co., Ltd. in China was used to trap the generated $^*\text{CH}_3$ or $^*\text{OH}$ radicals in the reaction. All of the reagents used in our experiments have analytical grade purity and were used without further purification. De-ionized water (H₂O) was obtained from a Millipore system.

2.2. Preparation of 1 T-OsCoTe₂ and 2 H-OsCoTe₂

To synthesize polycrystalline samples of 1 T-OsCoTe₂ and 2 H-OsCoTe₂, stoichiometric amounts of the constituent elements were weighted and grounded with mortar and pestle under inert atmosphere (glovebox). The reaction mixtures were then loaded into quartz tubes and subsequently sealed under vacuum (10^{-3} mbar). The synthesis of 1 T-OsCoTe₂ was performed via heating the evacuated quartz tubes at 1000 °C for 4 h with a heating rate of 5 °C·min⁻¹, subsequently the temperature was decrease to 800 °C at 5 °C·min⁻¹ and kept for 24 h. Finally, the mixtures were cooled to room temperature at 0.5 °C·min⁻¹. 2 H-OsCoTe₂ was synthesized by slowly heating the ampoule with the reaction mixture to 1000 °C, keeping it at 1000 °C for 5 days, and cooling the ampule slowly to room temperature over 1 day. In order to ensure the homogeneity of the samples, the obtained mixtures were reground and heated again at 1000 °C for 4 days. After cooling to room temperature, 2 H-OsCoTe₂ was obtained.

The 1 T-CoTe₂ and 2 H-CoTe₂ were prepared following the above synthesis steps of 1 T-OsCoTe₂ and 2 H-OsCoTe₂ without adding Os powder. The 2 H-OsTe₂ was prepared following the above synthesis

steps of 2 H-OsCoTe₂ without adding Co powder. It is worth to mention here that, to gain deeper insight of Te electron bridging characteristics, the pure OsCo alloys were prepared following the above synthesis steps of 1 T-OsCoTe₂ without adding Te powder.

2.3. Photocatalytic CO₂RR measurements

Photocatalytic CO₂RR measurement was conducted in an online trace gas analysis system with a gas chromatography-mass spectrometry (GC-MS, Agilent GC/MS-7000D) and ¹H nuclear magnetic resonance (¹H NMR) spectroscopy. Firstly, 50 mg of photocatalyst and 100 mL of aqueous acetonitrile (MeCN) solution [13] were added in the Pyrex glass reaction cell with sonication. Then, the reactor system was then filled with pure CO₂ gas (80 kPa) following complete evacuation. After adsorption equilibrium, the reactor system was put under a simulated light source which was provided by a 300 W Xe lamp (Beijing Perfect-light, Microsolar 300, 100 mW cm⁻²) with a UVCUT-420 nm filter to cut-off the light with wavelengths lower than 420 nm (i.e. $\lambda > 420$ nm), and the chilled water controlled the system temperature. Finally, the gas and liquid produced were analyzed every 1 h through GC-MS and ¹H NMR spectroscopy (Bruker AVIII HD 600), respectively. Notably, for the ¹H NMR measurement, 0.5 mL of the product solution was mixed with 0.1 mL of D₂O and 10 μL of dimethylsulfoxide (DMSO, as the internal standard). In addition, all the experiments were repeated at least 3 times in parallel to obtain an average value and error bars indicate standard deviations.

2.4. Characterization

Powder X-ray diffraction (PXRD) patterns were collected on an X-ray diffractometer (X' Pert3 Powder) equipped with a Kratky block-collimation system at 25.0 ± 0.1 °C and a sealed-tube X-ray generator with the Cu target operating at 45 kV and 40 mA. Inductively coupled plasma optical emission spectrometer (ICP-OES) was tested on an Agilent 7500cx instrument with an attached laser ablation system. UV-Vis-NIR diffused reflectance spectra (DRS) was collected on a spectrophotometer (UV-3100, Shimadzu, Japan) with BaSO₄ as the background holder. Steady-state photoluminescence (PL) and time-resolved PL (TRPL) measurements were performed on a Hamamatsu instrument (Hamamatsu C5680, Japan), with an excitation wavelength of 320 nm. CO₂ adsorption isotherms were obtained at 25 °C via using a Quantachrome Autosorb-iQ adsorption analyzer after the degassing process at 200 °C for 12 h.

2.5. Computational method of charge distribution

All of the calculations are performed in the framework of the spin-polarized density functional theory with the projector augmented plane-wave method, as implemented in the Materials Studio 2019 and Vienna ab initio simulation package (VASP) [14]. The generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof is selected for the exchange-correlation potential [15,16]. The van der Waals interaction was taken into account using DFT-D3 method with Becke-Jonson damping dispersion correction [17,18]. The cut-off energy for plane wave was set to 400 eV. The energy criterion was set to 10^{-5} eV in iterative solution of the Kohn-Sham equation. The Brillouin-zone sampling was conducted using Monkhorst-Pack (MP) grids of special points with the separation of 0.04 \AA^{-1} . All the structures are relaxed until the residual forces on the atoms have declined to less than 0.02 eV \AA^{-1} . A Gaussian smearing of 0.05 eV was applied to speed up self-consistent field iteration. Data analysis and visualization are carried out with the help of VASPKIT, Materials Studio 2019, and VESTA. DFT + U approach [19] with $U = 3.3$ eV was considered to evaluate the influence of strongly correlated d electrons of Co and Os on the calculated free energies. Adsorption energy (E_{ads}) was defined as $E_{\text{ads}} = E_{\text{adsorbate/substrate}} - E_{\text{substrate}} - E_{\text{adsorbate}}$, where $E_{\text{substrate}}$ is

the total energy of substrate, $E_{[\text{adsorbate/substrate}]}$ is the total energy when carbon monoxide (CO), methane (CH_4), ethylene (C_2H_4) or C_3H_8 is adsorbed on the substrate surface, $E_{[\text{adsorbate}]}$ refers to the energy of CO, CH_4 , C_2H_4 or C_3H_8 . The Gibbs free energy change (ΔG) was defined as $\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S$, where ΔE is the energy difference between the reactants and product obtained through DFT calculations. ΔE_{ZPE} and ΔS are the changes in the zero-point energies (ZPE) and entropy. T represents the temperature and was set as 298.15 K.

3. Result and discussion

3.1. Structural characterization

Based on transmission electron microscopy (TEM) image, 1 T-OsCoTe₂ demonstrates a typical bulk-like structure and possesses abundant pores (Fig. 1a). Notably, energy-dispersive X-ray spectroscopy (EDS) mapping indicates that Co elements on 1 T-OsCoTe₂ are distributed around Os elements, and there are high-density bright spots on Te elements, implying atomically dispersed Co and Os species (Fig. 1b). Meanwhile, high-resolution TEM (HRTEM) image shows that the lattice spacings of 3.64 and 1.93 Å (Fig. 1e) correspond to (111) plane of 1 T-CoTe₂ and (311) plane of 2 H-OsTe₂, respectively (Fig. 1c). From the results, the phases of 1 T-CoTe₂ and 2 H-OsTe₂ belong to P-3m1 and Pa-3 space groups, respectively. This intuitive result provides direct evidence for successfully constructing 2 H-OsTe₂ and 1 T-CoTe₂ composite structures. To further confirm, an aberration-corrected high-angle annular dark-field scanning TEM (AC HAADF-STEM) image is employed and displayed two kinds of points with different brightness and colors through pseudo-color transformation (Fig. 1f and g). The HAADF-STEM

image of 1 T-OsCoTe₂ reveals a crystal structure resembling that of 1 T-CoTe₂ (P-3m1) and 2 H-OsTe₂ (Pa-3) (Fig. S1), with no discernible Os crystalline phase observed, potentially attributable to the low and uniform distribution of Os species (Fig. 1g). By comparing the magnified HAADF-STEM images, they match well with the lattice models after XRD optimization (Fig. S2). Selected regional electron diffraction (SAED) pattern shows diffraction rings and spots, suggesting polycrystalline and monocrystalline composite properties of 1 T-OsCoTe₂ (Fig. 1h). As an overall picture, the chemical composition of 1 T-OsCoTe₂ is quantitatively determined by ICP-OES results (Fig. S3a), which is similar to the chemical formula of 1 T-OsCoTe₂. Meanwhile, diffraction rings of 2 H-OsCoTe₂ can be observed in the SAED pattern, representing the polycrystalline property of 2 H-OsCoTe₂ (Fig. 1d and S3b–e).

3.2. Electronic structure analysis

The electronic structure information of 1 T-OsCoTe₂ and 2 H-OsCoTe₂ were compared via in-situ XPS spectra (Fig. 2 and S4). After 20 min of illumination, the binding energy of Co 2p shifts to the right via 1.97 eV, and then returns to the “dark-state” after 10 min of light-off, suggesting electronic gain of 1 T-CoTe₂ upon light illumination (Fig. 2a). This is mainly due to the electrons in the conduction band of 2 H-OsTe₂ being transferred to Co 2p orbitals on 1 T-CoTe₂ through a built-in electric field force [20,21], and the binding energy change of Os 4f on 2 H-OsTe₂ further confirms the direction of electron migration (Fig. 2b). Theoretically, the binding energy shift of Te 3d should be opposite to that of Os 4f on 2 H-OsTe₂. Nevertheless, this is not the case, and the binding energy of Te 3d shifts to the right by 3.02 eV after 20 min of light-on, and then to the left via 1.47 eV after 40 min of

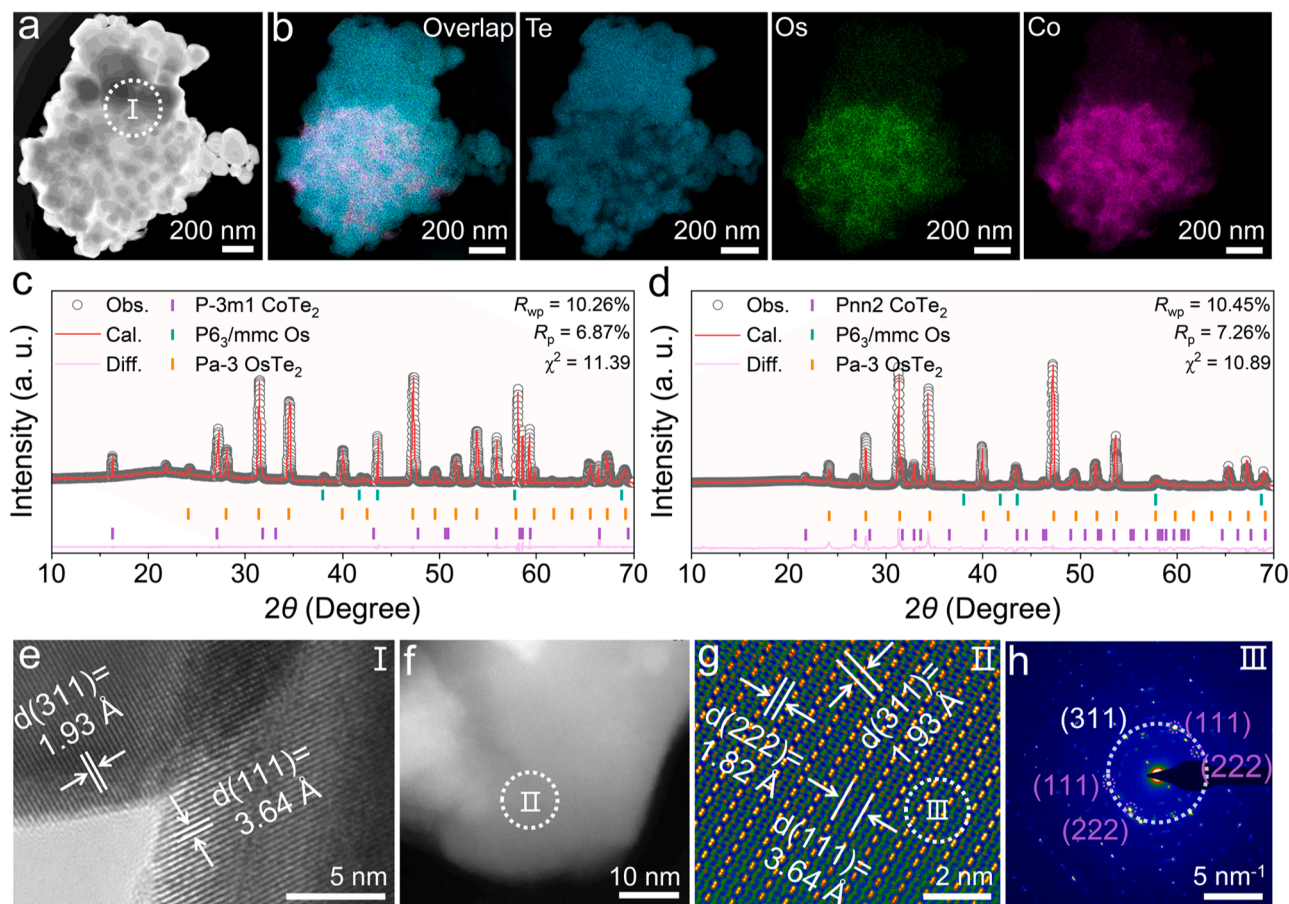


Fig. 1. (a) TEM and (b) EDS elemental mapping of 1 T-OsCoTe₂, respectively. XRD profiles and Rietveld refinement results of (c) 1 T-OsCoTe₂ and (d) 2 H-OsCoTe₂, respectively. (e) HRTEM image of 1 T-OsCoTe₂. (f,g) HAADF-STEM images and (h) SAED pattern of 1 T-OsCoTe₂, respectively.

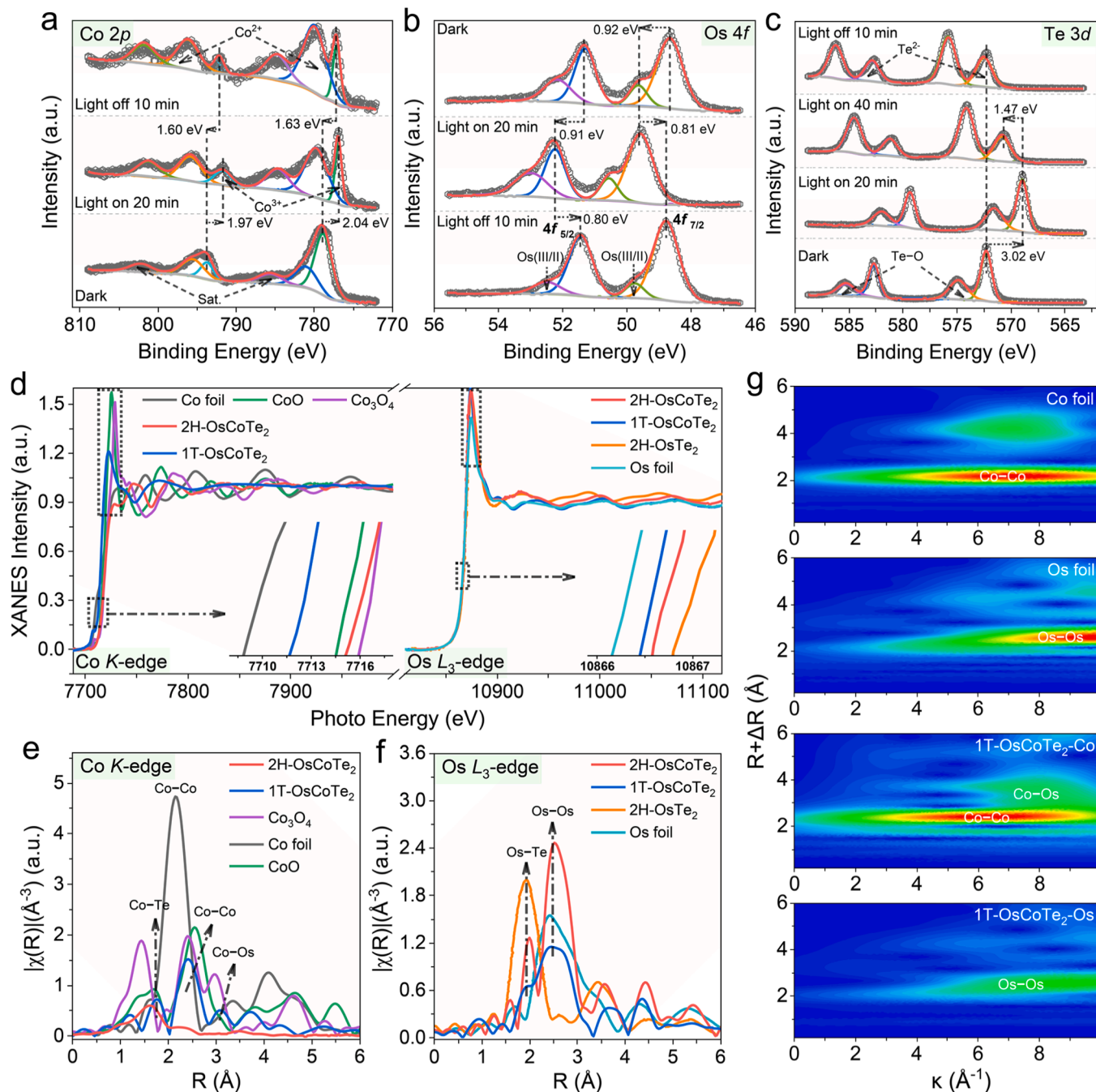


Fig. 2. In-situ XPS (a) Co 2p, (b) Os 4f, and (c) Te 3d spectra of 1 T-OsCoTe₂. (d) Co K-edge and Os L₃-edge XANES spectra of different samples. (e) Co K-edge and (f) Os L₃-edge EXAFS in R-space. (g) WT spectra for the κ^3 -weighted $\chi(\kappa)$ K-edge EXAFS signals of Co foil, Os foil, Co K-edge, and Os L₃-edge of 1 T-OsCoTe₂.

light-on. In sharp contrast, the binding energy of Te 3d does not completely return to the “dark-state” after 10 min of light-off (Fig. 2c) [22], which indicates that there are two electron transport processes in 1 T-OsCoTe₂ under light radiation. The first process is a direct electron transfer from Os atoms to Te atoms (i.e., causing to a decrease in the binding energy of Te 3d). The second process is an indirect electron transfer from Te atoms to Co atoms driven by an interfacial electric field (i.e., leading to an increase in the binding energy of Te 3d). The binding energy core-level peak for Te 3d does not shift, confirming that the two processes are balanced. Interestingly, the small changes in Os 4f binding energy before and after illumination disclose that the first electron transport process is the dominant one. The bulk electronic band structures and PDOS of 1 T-OsCoTe₂, 2 H-OsCoTe₂, 1 T-CoTe₂, and 2 H-CoTe₂ without spin-orbit coupling (SOC) were calculated as shown

in Fig S5 and S6. The few crossings and low PDOS at the Fermi level (E_F) of 1 T-CoTe₂ display its semimetallic properties. However, the PDOS at the Fermi surface in 1 T-OsCoTe₂ is clearly higher than that in 2 H-OsCoTe₂, indicating faster charge transfer and lower resistance of 1 T-OsCoTe₂ than 2 H-OsCoTe₂, which is in accordance with the transient photocurrents. In addition, the bulk electronic band structure (Fig S5a and b) denotes that the conduction and valence bands located near the E_F intersecting along G–L direction forms Dirac node, suggesting that 1 T-CoTe₂ possess ultra-high conductivity and mobility, which is a general feature of Dirac semimetal [6,7,23]. Thus, topologically protected surface states are accommodated at the 1 T-CoTe₂ (001) facet, which appear in the bandgap at the Γ point, as demonstrated in Fig S6a and c. Notably, the presence of TSSs was found in the surface energy bands of 1 T-CoTe₂ (001) with surface state energy levels near the E_F

(~ 0.01 eV higher) (Fig. S5b and e–i) [24], which means that non-trivial TSSs can provide additional electrons and facilitate the electrons transfer of Os–Te–Co electron bridging from the surface of 1 T-OsCoTe₂ to the adsorbed CO₂ molecules, which is conducive to CO₂RR.

To systematically explore the active sites of the photocatalysts as well as the coordination environments of Os and Co atoms, XAFS spectroscopy was implemented for 1 T-OsCoTe₂ and 2 H-OsCoTe₂. X-ray absorption near-edge structures (XANES) of Co *K*-edge indicate that the absorption edge of 2 H-OsCoTe₂ is located between CoO and Co₃O₄, meaning that the valence of Co element is between +2 and +3 [25]. The enlarged profile clarifies that the valence state of the Co element in 2 H-OsCoTe₂ is close to +2. Meanwhile, XANES spectra of Os *L*₃-edge show that the positions of the absorption threshold of 1 T-OsCoTe₂ and 2 H-OsCoTe₂ are situated in Os foil and 2 H-OsTe₂ (Fig. 2c), which reveals that the valences of Os element are between 0 and +2 [26]. Extraordinarily, the intensity of the white-line peak of Co *K*-edge XANES spectrum of 1 T-OsCoTe₂ is lower than that of CoO, indicating a decrease in the PDOS and an increase in the electron filling of the *d*-band for the unoccupied state of Co 3*d* near the Fermi energy level. This result suggests that electrons are injected into the Co 3*d* orbitals after introducing 2 H-OsTe₂ [27,28]. Contrastingly, the white-line peak intensity of Os *L*₃-edge XANES spectrum of 1 T-OsCoTe₂ is higher than that of 2 H-OsTe₂. Moreover, the intensity of white-line peak and absorption edge of 1 T-OsCoTe₂ are significantly different from that of Os foil, while it is extremely close to that of 2 H-OsTe₂ (Fig. 2c), which suggests that the average Os valence state of 1 T-OsCoTe₂ is similar to that of 2 H-OsTe₂, agreement with XPS results [26,29]. It is estimated that Co atoms sequentially form electron accumulation layers by swiping electrons from the surrounding Os atoms through Co–Te bonds. Significantly, the charge density around the Co atoms increases, further demonstrating the electron-donating nature of Os–Te bonds. As displayed by the PDOS in Fig. S6d and e, the higher electron density around the Co atoms modulates the 3*d* orbital structure, leading to a positive shift in the center of the *d*-band. The resulting electron-deficient Os atoms bring the whole 1 T-OsCoTe₂ close to a relatively high valence state, which can be further verified from the results of Os *L*₃-edge *k*²-weighted oscillation (Fig. S6f). The first significant peak in EXAFS spectra of 1 T-OsCoTe₂ (Fig. 2d) denotes that Co atoms are coordinated with Te atoms nearest neighboring shell locates at ~ 1.76 Å, referring to the peak of Co–Te bonds in 1 T-CoTe₂ [30]. Simultaneously, the first significant peak can be attributed to Os–Te bonds that Os atoms are coordinated through Te atoms nearest neighboring shell at ~ 1.93 Å, which is well consistent with that of 2 H-OsTe₂, indicating that Os atoms interact with Te atoms through Os–Te bonds (Fig. 2e). The detailed coordination environments of Co and Os atoms were further investigated by Fourier transform of extended X-ray absorption fine structures (EXAFS) and wavelet transforms (WT) spectra (Fig. 2f and g). The second prominent peak at ~ 2.59 Å in Os *L*₃-edge EXAFS spectrum of 1 T-OsCoTe₂ can be attributed to Co–Os coordination at the first shell, which is similar to 2 H-OsCoTe₂ and different from that of Os–Te coordination. Of note, no significant peaks such as Os–Os (~ 2.68 Å) are detected on the longer backscattering paths (Fig. S7 and Table S1), indicating Os species in 1 T-OsCoTe₂ and 2 H-OsCoTe₂ exist in a single atomic state [26,31], which is consistent with XRD fitting results. Collectively, after the formation of 1 T-OsCoTe₂, the number of electrons on Co atoms increases and the number of electrons on Os atoms decreases, and there may be transferred from Os to Co via Os–Te–Co electron bridging.

3.3. Photocatalytic CO₂RR performance

The CO₂ photoreduction products were measured in MeCN aqueous solution (MeCN:H₂O = 6:1, Fig. S8a) to evaluate CO₂RR performance of the catalyst [13,32,33]. 50 mg of photocatalyst loading was adopted to improve C₃H₈ selectivity (Fig. S8b). A similar photocatalyst dosage was often used in previous photocatalytic works. The gaseous and liquid

reduction products were analyzed and quantified via GC-MS and ¹H NMR spectroscopy, respectively (Fig. 3a and S9a–d). CO and CH₄ are mainly detected on 1 T-CoTe₂, 2 H-OsTe₂, and OsCo with yields of 33.74, 23.61, and 11.3 μmol g^{−1} h^{−1}, respectively (Fig. 3a). 1 T-OsCoTe₂ exhibits significant yields of C₂H₄ (3.26 μmol g^{−1} h^{−1}) and C₃H₈ (10.28 μmol g^{−1} h^{−1}), together with a small amount of CH₄ (1.78 μmol g^{−1} h^{−1}), in addition to CO (14.91 μmol g^{−1} h^{−1}) (Fig. 3b and c), exhibiting an exceptionally strong C–C coupling capability [34]. The C₂H₄ and C₃H₈ yields of 2 H-OsCoTe₂ are reduced to 2.27 and 7.72 μmol g^{−1} h^{−1}, indicating that the non-trivial TSSs of 1 T-OsCoTe₂ is conducive to the improvement of CO₂ activity through enhancing the adsorption of intermediates, promoting carrier mobility and reducing the activation energy of reactants [4,5]. Strikingly, an IQE_{cr} of 1 T-OsCoTe₂ at the wavelength of 380, 400, 420, 440, 460, 480, 500, and 520 nm is 54.6%, 25.63 %, 10.84 %, 9.49 %, 7.12 %, 5.25 %, 2.80 %, and 1.27 %, respectively (Table S2) [35,36]. A high product-based selectivity of C₃H₈ of 34.0 % is achieved (71.20 % of the electron-based selectivity), and that of total C₂₊ hydrocarbons is as high as 44.8 % (84.7 % of the electron-based selectivity) (Fig. 3b) [37]. The catalytic activity of 1 T-OsCoTe₂ and 2 H-OsCoTe₂ is competitive with those of well-known photocatalysts under strict conditions (Table S3). Herein, we further tested the catalytic performance of 1 T-OsCoTe₂ and 2 H-OsCoTe₂ in pure H₂O (with H₂O as the electron donor), and the results shows that the generation rate of all carbon-based products decreased (Fig. S10a). Moreover, the C₂₊ hydrocarbon selectivity of 1 T-OsCoTe₂ becomes lower in pure H₂O (Fig. S10b). Interestingly, no C₂₊ hydrocarbons of 2 H-OsCoTe₂ are detected in pure H₂O, but more H₂ is produced with a formation rate of 3.84 μmol g^{−1} h^{−1} (10.27 % of the electron-based selectivity) (Fig. S8c and d). The improvement of the catalytic activity and selectivity may be attributed to the high solubility of CO₂ in MeCN, which significantly increases the local accessibility of CO₂, thus enhancing the contact between 1 T-OsCoTe₂ and CO₂, and promoting C–C coupling [34]. Enlightened via the analyses described above, the effective inhibition of CO generation and increased C₂₊ hydrocarbons production on 1 T-OsCoTe₂ and 2 H-OsCoTe₂ confirm that the formation of C₂₊ hydrocarbons are probably owing to the C–C coupling depletion of *CO.

The gas production rate of 1 T-OsCoTe₂ under light irradiation was measured by cyclic tests, as shown in Fig. 3d and S11a–c, which is pivotal for evaluating the stability of the photocatalyst. The distinctive CO₂ photoreduction activity and high selectivity of C₃H₈ and total C₂₊ hydrocarbons are still well maintained after eight cycling tests of 40 h. This is further supported through XRD (S11d), XPS (Fig. S12) and XAFS (Fig. S13) spectra of 1 T-OsCoTe₂ after the stability tests. All the post-reaction characterizations indicate that 1 T-OsCoTe₂ has the excellent capability and stability to efficiently achieve the photoreduction of CO₂ to C₂₊ hydrocarbons. Moreover, the isotropic experiment was further carried out by employing ¹³CO₂ as a reactant to ascertain the carbon source of the products. ¹³CO₂ isotope labeling experiment and the time profile of the relative abundance of ¹³C labeled products confirm that the carbon source for CO(g) and other hydrocarbon products originates from the input CO₂(g) (Fig. S9c and d) [38,39]. To explore the role of Te atoms in 1 T-OsCoTe₂, OsCo was synthesized under the same conditions. In sharp contrast, OsCo is nearly photo-catalytically incapable toward CO₂RR (Fig. 3b), confirming that Os–Te–Co electron bridging of 1 T-OsCoTe₂ promote photocatalytic activity. To elucidate the change in the valence states and the local structures surrounding Os and Co atoms, XAFS experiments further were performed in detail (Fig. S14). Compared with 1 T-OsCoTe₂, both the valence states of Os and Co atoms shift to lower energy in OsCo. Co *K*-edge XANES curves show that the absorption edge of OsCo is between that of Co foil and 1 T-CoTe₂ (Fig. S14a), indicating that the valence state of Co atoms in OsCo is between 0 and +2, which may be caused by surface oxidation. Moreover, OsCo exhibits a lower intensity than 1 T-CoTe₂ (inset in Fig. S14a), implying that the introduction of Te atoms reduces the oxidation state of Co atoms in 1 T-CoTe₂ [40]. Meanwhile, EXAFS fitting shows that Co

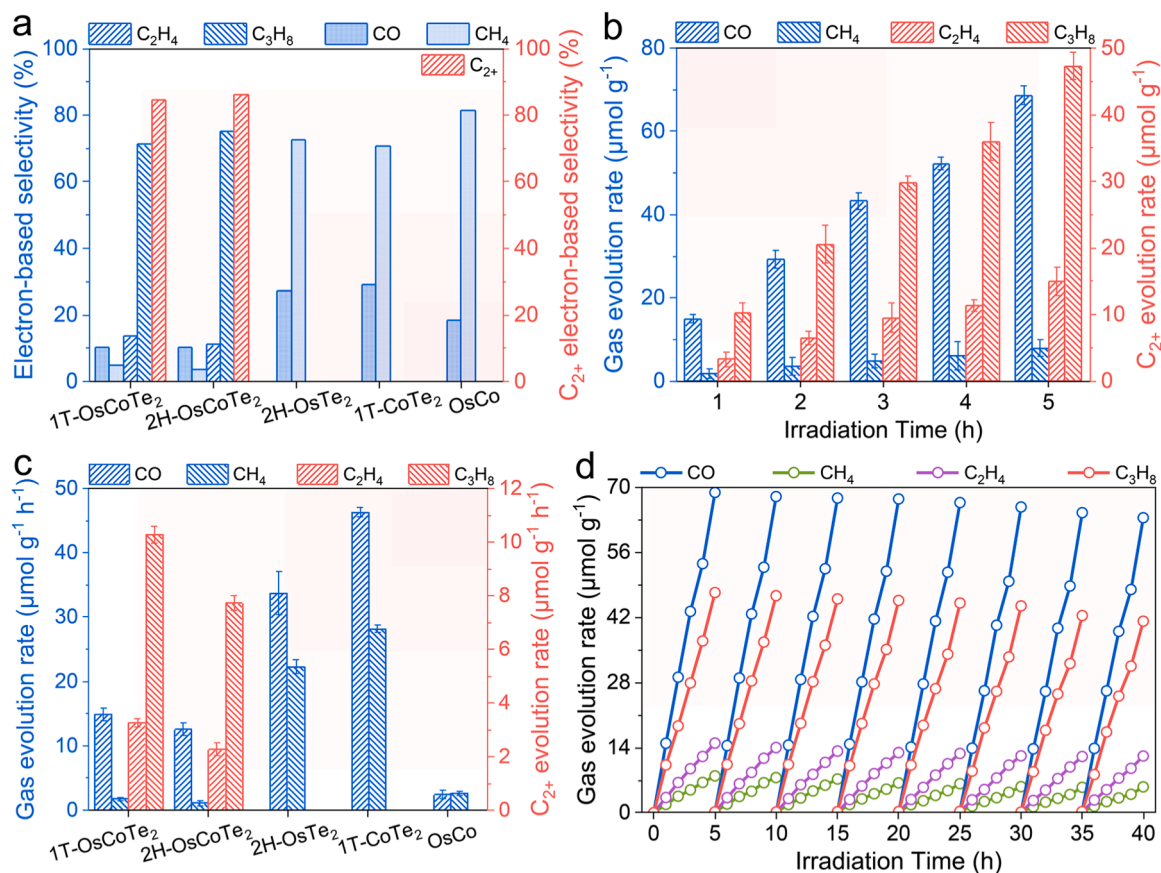


Fig. 3. (a) Electron-based selectivity on as-prepared samples in MeCN aqueous solution. (b) Photocatalytic product evolution as a function of light irradiation times on 1 T-OsCoTe₂ in MeCN aqueous solution. (c) Product formation rates on samples in MeCN aqueous solution. (d) Gas evolution amounts as a function of light irradiation time for 1 T-OsCoTe₂ over eight cycling tests in MeCN aqueous solution.

atoms in OsCo without the Te electron bridging is coordinated with Os atoms (Fig. S14b–f). As such, 1 T-OsCoTe₂ with Te electron bridging significantly accelerates photocatalytic CO₂ reduction to C₂₊ hydrocarbons.

3.4. Photoelectric performance analysis

The absorption edge of 1 T-OsCoTe₂ displays a blue shift compared with 2 H-OsCoTe₂ due to the non-trivial TSSs of 1 T-OsCoTe₂, while the light absorption is enhanced after implantation of 1 T-CoTe₂ (Fig. S15a). Transient photocurrent measurements confirm the enhanced charge separation and migration efficiency of 1 T-OsCoTe₂, ascribed to the non-trivial TSSs, which effectively shortens the charge transfer distance from body to surface and lowers charge recombination possibility (Fig. S15b). Theoretically, the fast charge carrier dynamics of 1 T-OsCoTe₂ is kinetically favorable for the multi-electron reactions of generating C₂₊ hydrocarbons. Therefore, the photogenerated carrier separation efficiency was determined via steady-state PL, TRPL, and transient photocurrents. Dramatic PL quenching occurs on 1 T-OsCoTe₂ relative to OsCo, implying that the intrinsic radiative recombination of photogenerated carrier in 2 H-OsTe₂ has been substantially inhibited due to the promoted charge transfer through Os–Te–Co electron bridging (Fig. S15c). Moreover, the TRPL decay spectra recorded at the corresponding steady-state emission peaks illustrate that 1 T-OsCoTe₂ has a longer average lifetime (τ_{avg}) of charge carriers with respect to 1 T-CoTe₂ and 2 H-OsTe₂ (Fig. S15d and Table S5), meaning that there is efficient charge transfer in 1 T-OsCoTe₂ [41]. As shown in Figs. S15b, 1 T-OsCoTe₂ is favorable for charge separation from the enhancement of photocurrents. Peculiarly, the transient photocurrents density and PL density of 2 H-OsTe₂ are close to those of OsCo, illustrating that these

factors do not have much influence on the performance difference between 2 H-OsTe₂ and OsCo [42–44]. In contrast, the non-trivial TSSs of 1 T-OsCoTe₂ are better than those of 2 H-OsCoTe₂, and thus should be the reason for the relatively higher performance of 1 T-OsCoTe₂. Ultrafast femtosecond time-resolved transient absorption (fs-TA) spectroscopy provided evidence for the mechanism of photogenerated carrier transfer. As shown in Fig. 4a and b, TA spectra of 1 T-OsCoTe₂ and 2 H-OsCoTe₂ both demonstrate pronounced positive and negative absorption peaks at 440 and 493 nm, belonging to the excited state absorption (ESA) and ground state bleach (GSB), respectively [45,46], in which the GSB peak reflects the relaxation of the excited state. A redshift of GSB peak with pump-probe delay time can be observed in Fig. 4c and d, mainly due to the broad size distribution of Os atoms in 1 T-OsCoTe₂ and 2 H-OsCoTe₂, where the smaller Os atoms have the larger band gaps and faster exciton annihilation [47,48]. To deeply analyze the dynamic behavior of charge carriers, GSB and ESA decay kinetics curves of both 1 T-OsCoTe₂ and 2 H-OsCoTe₂ are shown in Fig. 4e and f, respectively, which indicate that the kinetic decays of GSB and ESA are significantly suppressed on the probing time scale. The clear negative absorption bands attributed to the GSB peak signal can be observed, which implies charge carrier transfer between Os–Te–Co electron bridging [49], agreeing with the results of in-situ XPS and XAFS.

3.5. Reaction mechanism analysis

To understand the mechanism of photocatalytic CO₂RR at molecular level, the possible intermediates were performed by in-situ DRIFTS technique. In the spectra (Fig. 5a, b and Fig. S16a), the peaks at 1409/1432 cm^{−1} belong to HCO₃[−] [50], while the peaks at 1276/1597 cm^{−1} is assigned to bidentate carbonates (b-CO₃^{2−}) [51,52]. In addition, a small

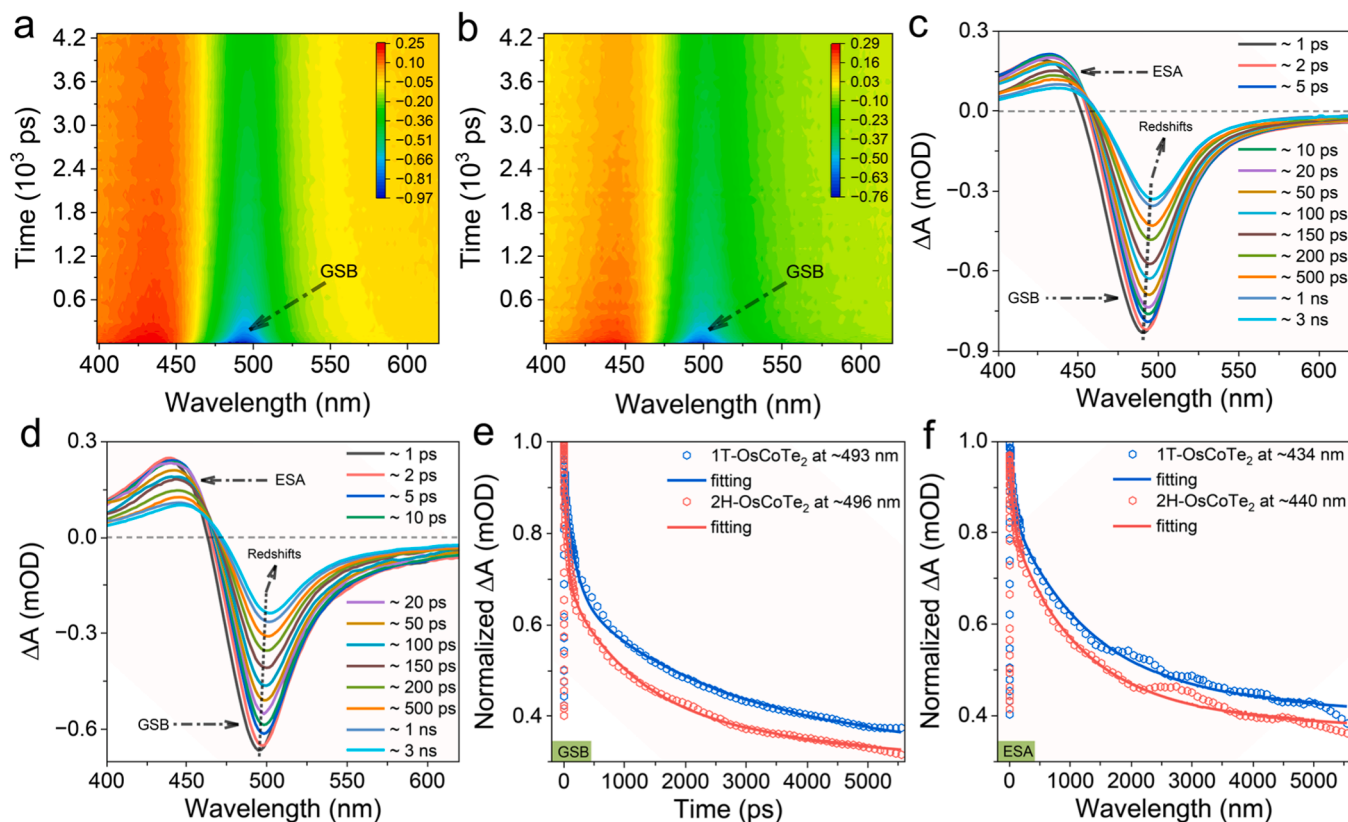


Fig. 4. 2D Pseudo-color images of (a) 1 T-OsCoTe₂ and (b) 2 H-OsCoTe₂ in ethanol solution after the excitation with a 310 nm laser pulse. The TA spectra of (c) 1 T-OsCoTe₂ and (d) 2 H-OsCoTe₂ at different delays time. (e) Comparison of decay kinetics and fitting lines for 1 T-OsCoTe₂ and 2 H-OsCoTe₂ taken through the GSB peaks at ~493 and ~496 nm, respectively. (f) Normalized decay kinetics and fitting lines for 1 T-OsCoTe₂ and 2 H-OsCoTe₂ taken through the ESA peaks at ~434 and ~440 nm, respectively.

amount of $^*\text{CH}_3$ (1473 cm^{-1}), $^*\text{CO}_3$ (1510 cm^{-1}), CH_3O^* (1127 cm^{-1}) [37], CHO^* (1044 cm^{-1}) and CH_2O^* (1711 cm^{-1}) is observed, resulting from the intermediates to the production of CH_4 (1352 cm^{-1}) and C_3H_8 [52,53]. The characteristic peaks of $^*\text{COOH}$ at 1563 and 1628 cm^{-1} appear as the most critical intermediates in the photoreduction of CO_2 -to- CO [13]. The increasing peak at 2130 cm^{-1} may be derived from $^*\text{CO}$, a key intermediate in the formation of CO . The peaks at 1980 and 2094 cm^{-1} are attributed to linear- and bridge-type CO adsorption at the Co sites, respectively (Fig. 5c). In addition, a new peak arising at 2126 cm^{-1} over 1 T-OsCoTe₂ and 1 T-CoTe₂ is attributed to the linear CO adsorption on the non-trivial TSSs (as mentioned in the introduction), demonstrating the well-formed TSS of 1 T-CoTe₂ in the samples [5]. Of note, a broad peak at 2039 cm^{-1} is observed, which belongs to bridge-type CO adsorption over 2 H-OsTe₂ [54], corresponding to the detection of carbonyl ($^*\text{COOH}$, $^*\text{CO}$, $^*\text{CHO}$, and $^*\text{CHOCO}$) intermediates via in-situ DRIFTS [55,56]. In-situ electron paramagnetic resonance (ESR) spectroscopy was used to further detect free radicals produced by photoinduced activation of various reactants. As shown in Fig. 5d, $^*\text{CH}_3$ is detected in addition to $^*\text{OH}$ when CH_4 is injected into an aqueous solution containing 1 T-OsCoTe₂ and 2 H-OsCoTe₂ under visible light illumination, $^*\text{CH}_3$, in addition to $^*\text{OH}$, are detected (Fig. S16b and c) [57,58]. In order to further understand CO_2 RR mechanism through elemental information, carbon and oxygen species on the surface of the material were also monitored by in-situ near ambient pressure XPS (NAP-XPS) measurements. As shown in Fig. 5e and S17, a peak of CH_4 (287.0 eV) is clearly detected in C 1 s XPS spectra (Fig. S17a). The C1s peaks of $^*\text{CH}_x$, C–O, and $^*\text{COO}$ species occurring at 285.4 , 286.1 , and 289.2 eV increase with the time evolution upon visible light irradiation. Afterward, it is further verified that CO_2 was reduced to produce oxygen-containing compounds via collecting the O 1 s spectrum in NAP-XPS. The characteristic peaks of $^*\text{OH}$ (531.1 eV), C–O (531.9 eV),

H_2O (532.6 eV), and C=O (533.3 eV) could be resolved under visible light illumination (Fig. 5f). Interestingly, strong $^*\text{CO}$ signals are observed with in-situ DRIFTS and NAP-XPS, but extremely little CO is detected on 1 T-OsCoTe₂ and 2 H-OsCoTe₂. Indeed, Fig. 5d already reflects the relatively strong adsorption of CO on the Co active sites, allowing $^*\text{CO}$ to couple to other intermediates before desorption [59, 60]. Taken together, the presence of $^*\text{CH}_x$, C–O, and $^*\text{COO}$ was confirmed by a series of in-situ tests, indicating that the co-adsorption reaction of CO_2 and H_2O on 1 T-OsCoTe₂ can generate a variety of surface carbonaceous intermediates (e.g., methyl and carbonyl) [54] and further C_{2+} hydrocarbons. The experimental results have revealed the critical role of 1 T-OsCoTe₂ in CH_4 -to- $\text{CH}_4/\text{C}_2\text{H}_4/\text{C}_3\text{H}_8$ conversion. Fig. 6a and b illustrate the proposed reaction pathway. CO_2 prefers to be activated at Os sites in the presence of H^+ and form $\text{Os}-\text{OCH}_3$. The $^*\text{CH}_3$ can be gradually converted to $\text{Os}-\text{O}$ through combining Te atoms from $\text{Os}-\text{Te}$ unit and the hydrogenation via H^+ (Fig. 6b). Simultaneously, the C_1-C_1 coupling between $^*\text{CHO}$ and $^*\text{CO}$ generates $\text{Co}-\text{CHOCO}$ at $\text{Co}-\text{Te}$ unit interface, and the further hydrolysis of $\text{Co}-\text{OCH}_2\text{CO}$ gives C_2H_4 as a product. The Os sites are also active for $\text{Os}-\text{CO}$ generation by directly oxidizing CO on $\text{Os}-\text{Te}$ unit (Fig. 6a). However, the $^*\text{CH}_3$ formed on $\text{Os}-\text{Te}$ unit can hardly approach $^*\text{CO}$ on $\text{Co}-\text{Te}$ unit, so the surplus $^*\text{CH}_3$ would evolve into CH_4 (Fig. 6b). Moreover, the formation of a five-membered ring between $^*\text{CH}_2\text{OCOCO}$ and Co active sites significantly mitigates the accumulation of localized electrons and weakens inter- and intramolecular electrostatic repulsion (Fig. 6a). The electronic and non-trivial TSSs, as well geometrical effects of 1 T-OsCoTe₂ may have jointly stabilized critical $^*\text{C}_{2+}$ intermediates and lowered their adsorption energy levels, thus facilitating C–C coupling [61–63].

To further probe the enhanced catalytic performance at the 1 T-OsCoTe₂, the CO_2 activation process is first analyzed. From CO_2 adsorption isotherms, 1 T-OsCoTe₂ has a CO_2 adsorption capacity of

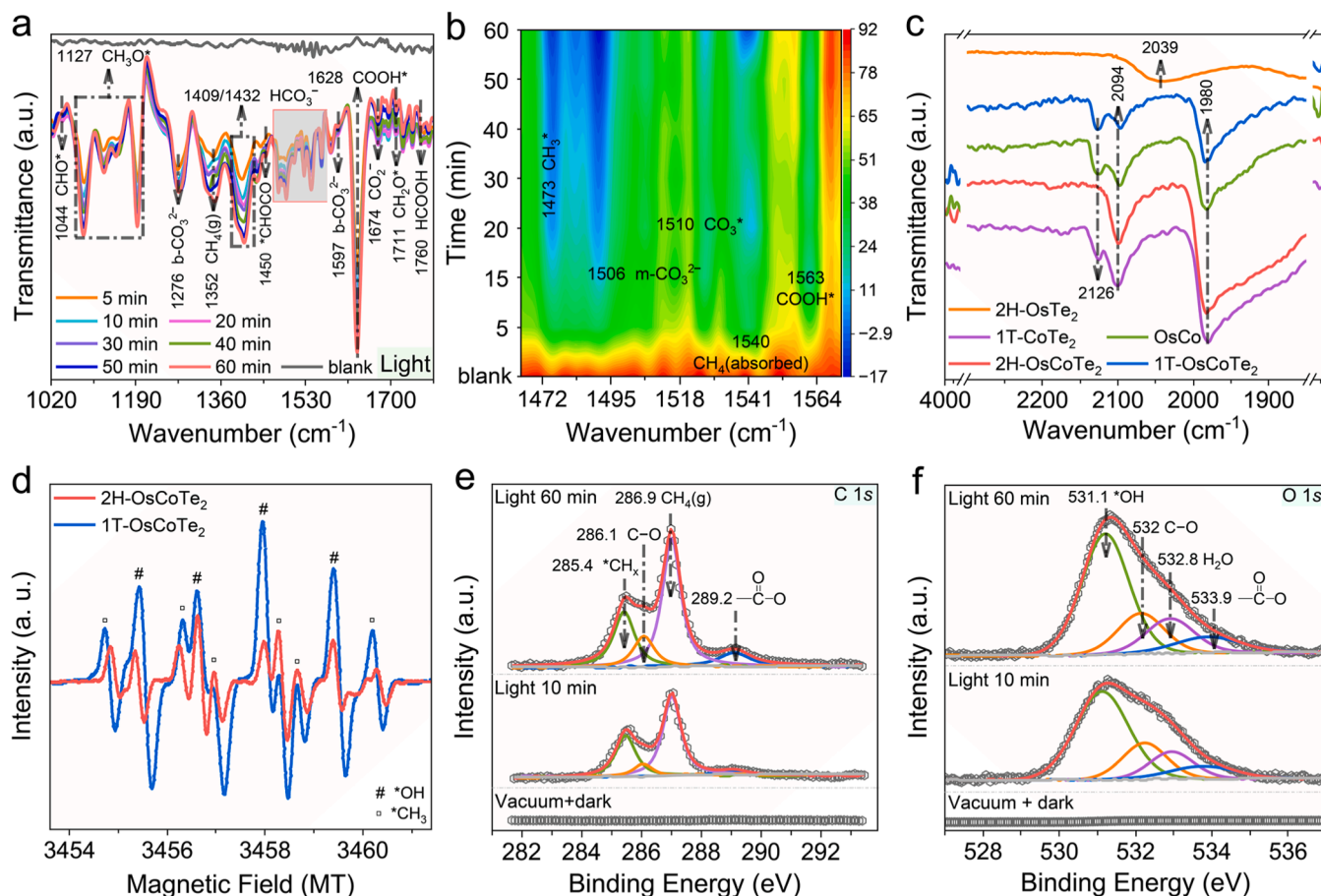


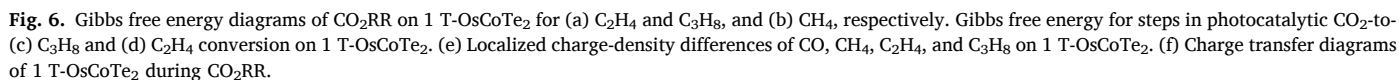
Fig. 5. (a,b) In-situ DRIFTS spectra for light-driven CO₂ conversion over 1 T-OsCoTe₂. (c) CO adsorption DRIFTS spectra of samples. (d) In-situ ESR spectra of CO₂ + H₂O mixture under light illumination at 298 K in the presence of DMPO over 1 T-OsCoTe₂ and 2 H-OsCoTe₂. In-situ NAP-XPS results of high-resolution (e) C 1 s and (f) O 1 s spectra over 1 T-OsCoTe₂.

49.69 cm³ g⁻¹ under 1.0 atm at 298 K, which is about 1.31 times larger than that of 2 H-OsCoTe₂ (37.91 cm³ g⁻¹, Fig. S18a). CO₂ adsorption isotherms reveal that 1 T-OsCoTe₂ possesses the highest CO₂ uptake capacity, which is the prerequisite step for triggering subsequent CO₂RR. Given that 1 T-OsCoTe₂ has a topological structure, this result suggests that the topological structure plays a crucial role in enhancing CO₂ adsorption capacity [13]. Benefiting from the microenvironment constructed via 1 T-CoTe₂, the optimal 1-OsCoTe₂ exhibits a high CO₂ adsorption capacity, which is favorable for the CO₂RR to C₂H₄ and C₃H₈. As revealed by in-situ characterizations, *COOH, *CO, *CHO, and *CHOCO species are the key intermediates for conversion of CO₂-to-C₂+ hydrocarbons, which is closely related to the presence of coupling *CO and Co sites in 1 T-OsCoTe₂. In order to further elucidate the intrinsic reasons for the excellent catalytic activity of 1 T-OsCoTe₂, to understand the nature of the photocatalyst active sites, and to analyze the reaction mechanism of coupling *CO in the C₃H₈ generation process, DFT calculations were carried out on the optimized 1 T-OsCoTe₂ and 2 H-OsCoTe₂ using the computational hydrogen electrode model (Fig. 6e, f, and S19) [34,64]. DFT calculation results show that *CO is difficult to desorb on 1 T-OsCoTe₂, rather than further hydrogenation or C-C coupling reaction, consistent with the result that CO is the major product on 1 T-OsCoTe₂ (Figs. 3c, 6c, and S20a). The absorbed CO₂ is firstly converted to *CHO through *COOH and *CO on 1 T-OsCoTe₂ (Fig. S18b-f). Then, *CHO at 1 T-OsCoTe₂ may couple with the CO diffusing from Co-Te unit to generate *CHOCO with a free energy change of -0.783 eV [55,65]. The C₁-C₂ coupling reaction (*CH₂OCO + *CO → *CH₂OCOCO) is thermodynamically calculated to be a self-reversing proceeding exergonic reaction (ΔG = -0.677 eV < 0)

[66]. It is worth noting that, on 2 H-OsCoTe₂, C₁-C₁ coupling is challenging due to the large variation uphill energy changes, resulting in the hydrogenation of *CO to CH₄ being preferred (Fig. S20b) [67,68]. Meanwhile, for 1 T-OsCoTe₂, some of *C₂+ species will continue hydrogenating through a series of proton-electron steps to form C₂H₄. The free energy changes of the rate-determining step (RDS) of C₃H₈ formation path (Fig. 6c) and C₂H₄ formation path (Fig. 6d) are calculated to be 1.623 and 1.98 eV, respectively, indicating that C₃H₈ is easier to generate than C₂H₄. This is consistent with our experimental results of outperforming C₃H₈ than C₂H₄ yields on 1 T-OsCoTe₂. The downslope energy change of C-C coupling on 1 T-OsCoTe₂ may be due to the low energy levels of *CHOCO and *CH₂OCOCO (Fig. S20c-e). The above analysis shows that both C₁-C₁ and C₁-C₂ coupling reactions are favorable on 1 T-OsCoTe₂, in contrast to 2 H-OsCoTe₂ and other reported catalysts with challenging C-C coupling.

4. Conclusion

A simple solid-phase strategy constructs 1 T-OsCoTe₂ topological semimetal, meanwhile, the CO₂RR properties and the function of Co and Os species in 1 T-OsCoTe₂ were systematically investigated. In-situ XPS and XAFS investigations reveal that Co and Os atoms coordinated with Te atoms enable an efficient site-to-site electron transfer to ensure the high efficiency of CO₂RR. Experimental evidence suggests a high electron-based selectivity of 71.2 % for C₃H₈ (product-based selectivity of 34.2 %) and 84.75 % for total C₂+ hydrocarbons (product-based selectivity of 44.79 %), as well as an IQE_{cr} of 54.6 % at 380 nm. An in-depth mechanism study illustrates that the synergistic effect of



CRediT authorship contribution statement

Lingyong Zeng: Methodology, Investigation. **Longfu Li:** Methodology, Investigation. **Chao Zhang:** Methodology, Investigation. **Kuan Li:** Methodology, Investigation. **Kai Yan:** Writing – review & editing, Project administration, Funding acquisition. **Kangwang Wang:** Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Huixia Luo:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Peifeng Yu:** Methodology, Investigation. **Mingjie Wu:** Methodology, Investigation. **Ying Liang:** Methodology, Investigation. **Hector F. Garces:** Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2024.124058](https://doi.org/10.1016/j.apcatb.2024.124058).

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